

## THE SERENDIPITOUS ASSOCIATION OF SEDIMENTARY BASINS AND GREENHOUSE GASES

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### INTRODUCTION

Sedimentary basins are the major world repository of fossil fuels—these include petroleum and natural gas, and coal. Industry has grown up over some of the sedimentary basins and in many cases is the source of major greenhouse gas emissions, the most important of which is  $\text{CO}_2$ . This is a relationship which might be expected. The realization that greenhouse gas emissions may be contributing to global warming has led to research into the mitigation of the effects of these emissions by natural processes, by use in manufacture of chemicals, and by disposal into oceans or sedimentary basins.

One of the more promising avenues of research has been into the disposal of  $\text{CO}_2$  into aquifers deep in sedimentary basins. Of the various methods that have been suggested for the disposal of  $\text{CO}_2$  in sedimentary basins (in geological structures such as salt domes, in depleted oil and gas reservoirs, in coalbeds, or in aquifers), only that in aquifers involving mineral trapping renders the  $\text{CO}_2$  harmless. There is an additional advantage because the volume of pore space available in deep aquifers far exceeds that of salt domes, depleted hydrocarbon reservoirs, or enhanced oil recovery projects. Further, aquifers are widely distributed and, very important, they underlie most point sources of  $\text{CO}_2$  emission. Carbon dioxide is an ideal candidate for aquifer disposal because of its high density and high solubility in water at the relatively high pressures that exist in deeper aquifers. This technology is economically viable and is in active development in areas as widely separated as the North Sea and Indonesia. Recently, a suggestion has been made that in addition to disposing of  $\text{CO}_2$  into aquifers, it may also be used to remove methane from deep coalbeds. The methane- $\text{CO}_2$  mixture would be separated at the surface and the methane used as fuel, in the normal way. While this would produce more  $\text{CO}_2$ , the solution to that problem is clear. The  $\text{CO}_2$  fraction of the gas that is returned to the surface could be re-used for more methane recovery or disposed of in deep aquifers. This recycling of gases is possible because there is a close association of the fossil fuel resources of sedimentary basins and the greenhouse gas emitting industry that is based on those fuels. We regard this as a serendipitous association.

### SEDIMENTARY BASINS AND FOSSIL FUELS

There is a natural association of sedimentary basins (which are accumulations of sedimentary rocks) and fossil fuels through the processes of (1) accumulation of organic matter in the original sediments, (2) its burial to depths where temperatures can change (mature) the character of the organic matter, and (3) in the case of petroleum and natural gas, which are fluids, create structures into which they can migrate and accumulate. These processes result in the development of fossil fuel deposits in the sedimentary basins, and the association is a natural one. Therefore, we should expect a relation between the sedimentary basin, the exploitation of its fossil fuels, and the resulting greenhouse gas emissions.

Despite the wide range of processes that may act on basins, the relation is strong. Any specific basin may be a prolific hydrocarbon producer or not, depending on its geological history. The age of the rocks will also play a part in determining the probability of oil, natural gas, or coal being present. Despite these variables, all sedimentary basins have a common feature in the nature of the fluid that effectively fills all the pore spaces—formation water—for oil and gas are rare fluids in terms of their volume in sedimentary basins, despite their dominant economic importance. The next part of this note deals with the processes that control the movement of formation water in sedimentary basins, because it is this fluid (and the space it occupies), and not oil and gas, that is important for aquifer disposal of  $\text{CO}_2$ .

### HYDROGEOLOGY OF SEDIMENTARY BASINS

It is important to understand that most sedimentary rocks contain pore space between the mineral particles, and the pores are filled with fluid, mostly formation water but occasionally hydrocarbons. Any joints, fractures or faults are also filled with formation water. The original pore space is reduced due to compaction by overlying sediments, but seldom does it disappear altogether even in the most deeply buried rocks. The pore space can also be reduced by the deposition of minerals from the formation water during diagenesis. Conversely, the formation water may be of such a composition as to dissolve minerals from the rock, perhaps even creating more pore space than in the original deposit. There is a chemical balance between the formation water and the rock, through water-rock interaction processes. This balance will be disturbed if  $\text{CO}_2$  is injected into the sedimentary rock.

Formation water and other fluids in sedimentary basins are in constant motion, though the rate of movement is generally slow; in the Alberta Basin it is of the order of 1–10 cm/year. Fluids move through the pore spaces of the rocks basically under two forces. In the early history of sedimentary basins the driving mechanism is compaction, with the direction of movement upward and toward the existing shoreline. Once the sedimentary rocks are uplifted, the fluids in the rocks come under the influence of the meteoric water system, and fluid movement in the rocks is controlled by the local topographic elevation. This means that, as

a general rule, major upland areas are regions of recharge and major lowlands are discharge areas. The internal flow system in sedimentary basins is governed by (1) differences in the ability of the different rock types to transmit water, (2) processes due to uplift and erosion that may counter the normal topographically controlled forces, and (3) buoyancy effects due to salinity contrast between formation waters. For our purposes, however, the important thing to remember is that all formation water is in motion, however slow.

Equally important is the fact that different sedimentary rocks transmit water to different degrees. The attribute that describes this ability to transmit water is called permeability. It is unrelated to the absolute porosity (or void space) of the rock, and reflects the degree to which the pores are interconnected; an isolated pore, no matter how large, cannot transmit water. Sedimentary rocks are therefore of three types, with respect to their ability to transmit water—aquifers, aquitards and aquicludes. Aquifers are rocks from which water can be pumped or into which water can be injected; examples include most sandstones and limestones. Aquitards allow movement of water through them over geological periods of time, but pumping and injection are not feasible; examples include shales. Aquicludes are barriers to water movement, and the best example is a salt bed. Note that these definitions are for any rock, so a highly fractured shale or granite can be a good aquifer, depending on the interconnectedness of the fractures. When any fluid is injected into an aquifer it will move out from the injection well under the influence of the imposed pressure. It is important to determine the rate of movement of the injected material and the path that it may be expected to follow. It is the task of the hydrogeologist to determine the natural, undisturbed hydrogeological regime, and then see how the injected material will perturb the natural system. In conjunction with the geochemist, it is possible to predict the effects resulting from the injection of  $\text{CO}_2$  into deep aquifers in a sedimentary basin.

#### AQUIFER DISPOSAL OF $\text{CO}_2$

The most comprehensive evaluation of the aquifer disposal of  $\text{CO}_2$  is that carried out by the Alberta Research Council in the Alberta Basin—summarized in Hitchon (1996 and references therein). There are two ways in which  $\text{CO}_2$  can be trapped in aquifers: (1) hydrodynamic trapping and (2) mineral trapping. At their most fundamental, these concepts refer to the injection of liquid  $\text{CO}_2$  into aquifers, at least 800 m deep, in sedimentary basins, and into situations that either (1) trap the  $\text{CO}_2$  into flow systems for geological periods of time (hydrodynamic trapping) or (2) convert the  $\text{CO}_2$  to carbonate minerals and thus render it immobile (mineral trapping).

Aquifers suitable for injection of  $\text{CO}_2$  must satisfy the following general conditions: (1) the top of the aquifer must be > 800 m deep (at this depth the  $\text{CO}_2$  will be in a supercritical state); (2) the aquifer should be capped by a regional aquitard (sealing unit); (3) the aquifer should have enough porosity and adequate permeability; the near-well permeability should be high to allow good injection capability, but the regional permeability should be low so that the residence time of the  $\text{CO}_2$  is high; (4) the injection site should be close to the  $\text{CO}_2$ -emitting source.

The strategy is therefore: (1) to identify the point sources of  $\text{CO}_2$  emission; (2) to carry out a detailed, regional-scale hydrogeological analysis of the basin to identify suitable disposal aquifers that satisfy the conditions of depth, capping, permeability and storage capacity; and (3) to carry out detailed hydrogeological, injectivity and geochemical studies for the identified aquifers in the immediate vicinity of the  $\text{CO}_2$  sources.

##### *Hydrodynamic Trapping*

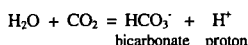
When  $\text{CO}_2$ , or any fluid, is injected into an aquifer at an appropriate pressure below the fracture pressure, it moves out from the injection well and flows with the natural flow regime. For the Alberta Basin, simple calculations show that times of the order of millions of years will still find the  $\text{CO}_2$  within tens of kilometers of the injection site. This geological time-scale trapping of  $\text{CO}_2$  in deep regional aquifers as a result of very low flow velocity is called hydrodynamic trapping because it depends on the hydrodynamic regime of the formation waters. Some  $\text{CO}_2$  will dissolve in the formation water and travel as a dissolved phase; this allows the processes of diffusion, dispersion and convection to be brought into play. In the Alberta Basin the main transport mechanisms for dissolved  $\text{CO}_2$  are molecular diffusion and dispersion; this means that the dissolved  $\text{CO}_2$  will spread laterally over a larger mass of rock than if convection was the main transport mechanism, leading to an increased sweep efficiency.

In contrast with  $\text{CO}_2$  injection in depleted oil and gas reservoirs, injection into deep aquifers in sedimentary basins has the advantage that it is not limited by reservoir location, size and properties. Thus there are many aquifers in the Alberta Basin suitable for  $\text{CO}_2$  disposal; some thin, isolated aquifers in the Cretaceous and post-Cretaceous sedimentary succession in the southwestern part of the basin have the additional significant property that the flow of formation water is down-dip, basin-inward, toward hydraulic sinks created by shale elastic rebound as a result of Tertiary-to-Recent erosion. Thus disposal of  $\text{CO}_2$ —and of any other liquid wastes—in these aquifers in this area will lead to the permanent capture and retention of  $\text{CO}_2$  and other wastes (on a geological time scale).

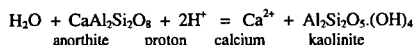
##### *Mineral Trapping*

The chemistry of formation water and rock mineralogy play an important part in determining the potential for  $\text{CO}_2$  capture through geochemical reactions. Most important, these reactions sequester the  $\text{CO}_2$  in immobile form as carbonate minerals.

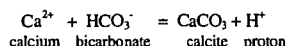
The dominant volatile components that affect mineral dissolution/precipitation reactions are  $\text{CO}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{SO}_2$  and  $\text{O}_2$ . These gases dissolve in the aqueous phase and alter the pH through reactions coupled to the dissociation of water. Reactions of the following type occur when  $\text{CO}_2$  dissolves in water:



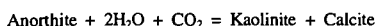
So, initially, some of the  $\text{CO}_2$  is held in the aqueous phase as bicarbonate. Only minor amounts of bicarbonate ion and the proton will be produced, no matter how high the pressure of  $\text{CO}_2$ . This is the reason that formation waters alone are not acceptable sinks for  $\text{CO}_2$ . However, the proton results in acid conditions in the water and, therefore, the possibility of attack on the silicate minerals present in the aquifer. The attack results in free ions of elements such as Ca, Mg, and Fe being released:



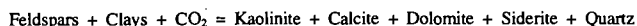
One of the fastest geochemical reactions is the precipitation of calcium carbonate, which occurs when free Ca ions exist in the presence of bicarbonate ions. The reaction produces calcite, and it is this reaction that forms the theoretical basis for the sequestering of the  $\text{CO}_2$  as the mineral calcite.



The overall result is just the sum of these three reactions:



There are similar reactions for the formation of calcium-magnesium carbonate (dolomite) and iron carbonate (siderite). For the more complex minerals commonly found in aquifers, the reaction is of the form:



where the  $\text{CO}_2$  is permanently fixed as the carbonate minerals calcite, dolomite and siderite. Mineral traps of  $\text{CO}_2$  are most effective when the aquifer contains minerals that are proton sinks—that is, the basic silicate minerals such as the feldspars and clay minerals. Consequently, mineral trapping of  $\text{CO}_2$  is favoured in sandstone aquifers over carbonate aquifers.

In the Glauconitic Sandstone aquifer of the Alberta Basin, the process of mineral trapping was examined using a water-rock reaction computer model, PATHARC.94. Based on aquifer mineralogy and estimated grain size, and using a formation water from the same aquifer, injection of  $\text{CO}_2$  into the Glauconitic Sandstone aquifer was modelled under reservoir conditions. The times for reacting out for the various minerals are: kaolinite 80 years; biotite (as an analogue for glauconite) 100 years; albite (Na-feldspar) 540 years; and K-feldspar 820 years. The resulting mineral assemblage will consist of quartz, and significant amounts of muscovite and siderite. Calculations show that there will be complete equilibrium in 820 years, resulting in the trapping of 6.2 moles of  $\text{CO}_2$  relative to each kilogram of formation water in the aquifer.

In summary, in the Alberta Basin, suitably located injection sites far from the basin edge and injection at depths > 800 m result in geologically long times before breakout to the surface occurs—if at all. By that time, if mineral trapping has not occurred, the pressure of  $\text{CO}_2$  will have been reduced to such an extent (from the original injection pressure) due to solution, diffusion and dispersion that the breakout will be a harmless event, occurring over a much longer period than the original injection period.

#### CARBON DIOXIDE, AQUIFERS AND SEDIMENTARY BASINS

Carbon dioxide disposal into low permeability, deep aquifers in sedimentary basins has been shown to be technically feasible and perhaps offers the largest potential for the landlocked areas of the world. A preliminary economic assessment indicated that significant costs will be incurred due mainly to  $\text{CO}_2$  capture, purification and compression, and secondarily due to the field facilities required. Despite these expenses, a recent report on the Sleipner Vest Field in the North Sea indicates that the 9.5%  $\text{CO}_2$  will be reduced to 2.5% in the sales gas, with about 1 million tonnes per year of the waste  $\text{CO}_2$  being injected into Tertiary sandstones; injection is scheduled to start 1996-10-01. An even larger project is the proposed removal of the 71%  $\text{CO}_2$  in the natural gas of the Natuna Field in Indonesia—one of the largest gas fields in the world with reported 1270 billion  $\text{m}^3$  of recoverable hydrocarbon reserves. It is proposed to inject the waste gas into two carbonate aquifers near the field; construction of the facilities is scheduled to last eight years.

The work reported for the Alberta Basin has demonstrated the concepts of hydrodynamic and mineral trapping of  $\text{CO}_2$  injected into deep aquifers using information based on a real situation. The capacity of the Alberta Basin aquifers for storage of  $\text{CO}_2$  exceeds 20 gigatonnes. The procedures and method of conducting a hydrogeological evaluation of a potential injection site can be emulated world-wide, as can the geochemical modelling. The numerical modelling resulted in nomograms specific to the Alberta Basin, but these nomograms are also viable in other world basins where the basin and reservoir data are similar. Not all sedimentary basins are suitable for injection of  $\text{CO}_2$ —some because their basin architecture is not suitable, others because they are remote with respect to both distance and appropriate point concentrations of  $\text{CO}_2$  emissions. Nevertheless, the results can be used in many world sedimentary basins which are in areas with

fossil fuel exploitation. The Sleipner Vest and Natuna examples cited above indicate that injection of  $\text{CO}_2$  into aquifers is now a practical process in the petroleum industry and economically viable. The conclusion of the Final Report of the Joule II Project, *The Underground Disposal of Carbon Dioxide*, is that underground disposal is a perfectly feasible method of disposing of very large quantities of  $\text{CO}_2$ , such as are produced by fossil fuel fired power plants and most other large point sources of  $\text{CO}_2$  (Holloway *et al.*, 1996). The same authors conclude that the next major step in implementing  $\text{CO}_2$  storage from power plants should be the demonstration of the storage process. The Sleipner Vest and Natuna projects are essentially large-scale demonstrations of the practicality of the underground disposal of  $\text{CO}_2$ . It is in this context that the Alberta study (Hitchon, 1996) is offered for world-wide application as an example of the methodology developed to prove the concept of hydrodynamic and mineral trapping of  $\text{CO}_2$  in aquifers.

#### COALBED DISPOSAL OF $\text{CO}_2$

Water and gases are generated during the conversion of plant material to coal, and they are either adsorbed onto the coal or are dissolved into the pore spaces. Methane is the dominant gas (about 95%), with the remaining gases including ethane,  $\text{CO}_2$ ,  $\text{N}_2$ , He and  $\text{H}_2$ .  $\text{H}_2\text{S}$  is found only in trace amounts, even in high-S coals, a factor that is related to the nature of the S in coals. The amount of methane formed can be related to the maturity of the coal. The methane associated with coalbeds is termed coalbed methane (CBM).

The attraction of disposing of  $\text{CO}_2$  in coalbeds is that it can be coupled directly with the production of methane, a fossil fuel (Gunter *et al.*, 1996). Unlike aquifer disposal of  $\text{CO}_2$ , the status of research on the recovery of methane from coalbeds using  $\text{CO}_2$  is at an embryonic stage. It has been known for two decades that  $\text{CO}_2$  is very effective in displacing methane from crushed coal under laboratory conditions; initially, this work was mainly aimed at improving the safety of coal mining. In the late 1980s, through a series of patents, Amoco Corporation demonstrated the potential use of  $\text{CO}_2$  and other gases to produce methane from deep coalbeds that are considered unmineable for technological or economic reasons. The injected  $\text{CO}_2$  is trapped by sorbing to the coal, thereby displacing the methane which flows to the production well. In 1995, Amoco started their first of a series of three nitrogen pilots, with an additional  $\text{CO}_2$ -pilot to be tested in the field in 1996.

Conventional or primary CBM recovery has been a practical operation in several coal-fields around the world, most notably in the USA. The process effectively involves the depressuring of the coalbed, which releases the adsorbed methane, as well as methane dissolved in the formation water. Although the method is conceptually simple, there are problems with recovering the methane at the imposed reduced pressure. This results in a delay in methane production and there are large amounts of formation water produced—that must be disposed to the subsurface. The disposal of  $\text{CO}_2$  in these methane-rich coalbeds partially solves these problems by (1) increasing the drive pressure, (2) sorbing the  $\text{CO}_2$  onto the coal and thereby driving off the methane, hence increasing the rate and the amount of methane produced, and (3) decreasing the relative rate of water production. Consequently, it is expected that this new technology will considerably increase the CBM reserves available for exploitation in North America. The fact that the coalbeds retain most of the  $\text{CO}_2$  injected is an additional environmental benefit.

The bulk of the CBM in Canada lies in the Alberta Basin. There is CBM production from many different coal basins in the USA, but around 96% comes from just two—the San Juan Basin, located in southwestern Colorado and northwestern New Mexico, and the Black Warrior Basin in Alabama. Estimates of the CBM resource in North America vary greatly, but by all reasonable estimates, a huge amount exists. In the USA, estimates of CBM resources range from 275 to 649 TCF; in Canada there is considerable more uncertainty, and estimates range over an order of magnitude, from 200 to 3000 TCF.

Experimentally, measured adsorption isotherms for binary and ternary mixtures of  $\text{CO}_2$ , methane and  $\text{N}_2$  show that the equilibrium gas and adsorbate phase compositions differ considerably, and that the total amount of gas mixture adsorbed is strongly dependent on composition and system. Carbon dioxide is the most strongly adsorbed gas, then methane, with  $\text{N}_2$  being the least adsorbed. The approximate adsorption ratios are 4:2:1; that is, 4 molecules of  $\text{CO}_2$  are adsorbed compared to 2 molecules of methane and 1 molecule of  $\text{N}_2$ , when comparing pure gases at the same temperature and pressure. Using a very conservative estimate of 150 TCF for the methane resource of the Alberta Basin, the total capacity for sorption by the deep coals of the Alberta Basin is approximately 10 gigatonnes of  $\text{CO}_2$ —very similar to that estimated for the aquifers of the Alberta Basin.

There is no reported field evaluation such as was carried out by the Alberta Research Council for aquifer injection of  $\text{CO}_2$  in the Alberta Basin. However, what work has been done suggests that the concept of disposing of  $\text{CO}_2$  or flue gas (a mixture of  $\text{N}_2$  and  $\text{CO}_2$ ) from the waste stream of power plants into coalbeds has considerable merit. An evaluation similar to that for aquifer  $\text{CO}_2$  disposal is currently being carried out for the Alberta Basin.

#### CONCLUSIONS

Sedimentary basins, fossil fuel resources, and deleterious greenhouse gas emissions are all closely associated. To exploit the fossil fuels is to produce the greenhouse gases. This does not have to be so. The main greenhouse gas produced by the burning of fossil fuels is  $\text{CO}_2$ . Rather than discharge  $\text{CO}_2$  to the atmosphere, it has been suggested that it be either disposed of in deep aquifers in the same sedimentary basins from which the fuel was extracted, or it be injected into deep coalbeds in the same basins to release the adsorbed methane. The former concept has been evaluated by the Alberta Research Council using field data from the Alberta Basin. Similar methodology is proposed for the Sleipner Vest Field in the North Sea,

and for the Natuna Field, Indonesia. Unlike aquifer disposal of  $\text{CO}_2$ , injection into coalbeds is not as technologically advanced. However, the concept appears viable, and a proof of concept study is being carried out for the Alberta Basin.

This note has been concerned with two of the five methodologies available for the mitigation of  $\text{CO}_2$  emissions from the burning of fossil fuels by disposal in sedimentary basins. These two processes have much in common, and it is pertinent to close with a cartoon (Figure 1) that outlines their main features. Compared to the other three technologies, the two discussed at length in this note potentially can trap much larger volumes of  $\text{CO}_2$ . The association of sedimentary basins, fossil fuel resources and the mitigation of greenhouse gas emissions from the burning of the fuels is indeed serendipitous.

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## $\text{CO}_2$ Disposal in Aquifers and Coalbeds

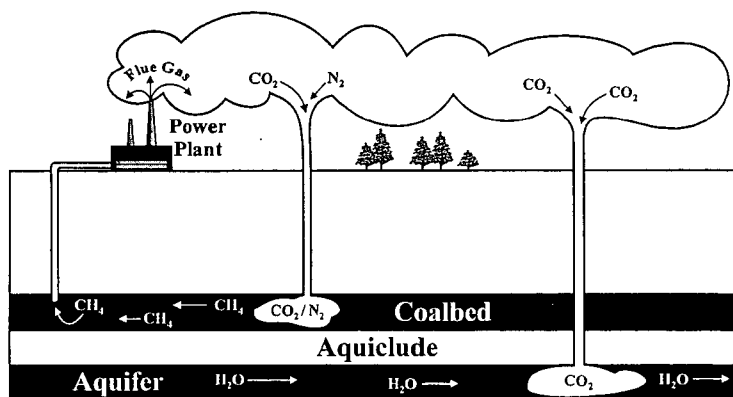


Figure 1. Cartoon showing the relation among sedimentary basins, fossil fuel resources, and the mitigation of  $\text{CO}_2$  emissions from the burning of fossil fuels by injection into deep aquifers and the recovery of methane from coalbeds.